

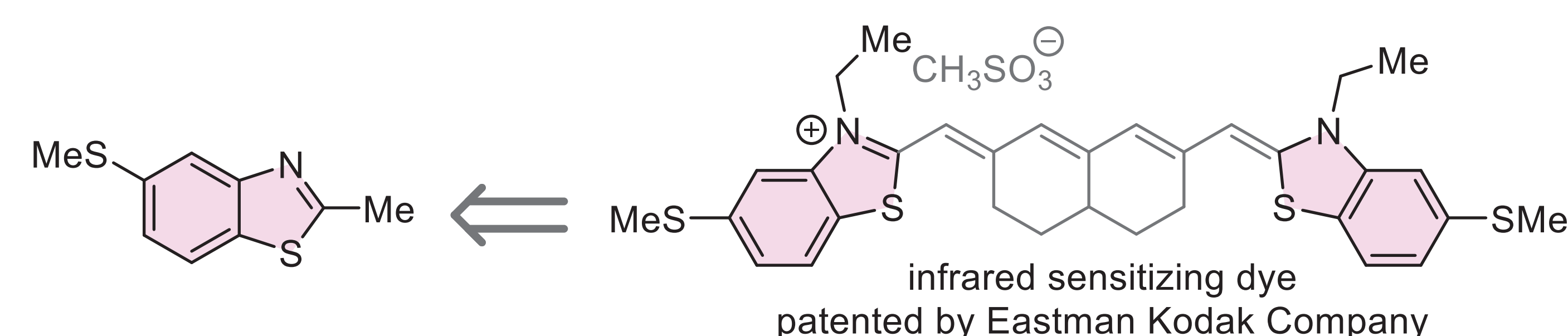
Semi-industrial synthesis of 2-alkyl-substituted benzothiazoles



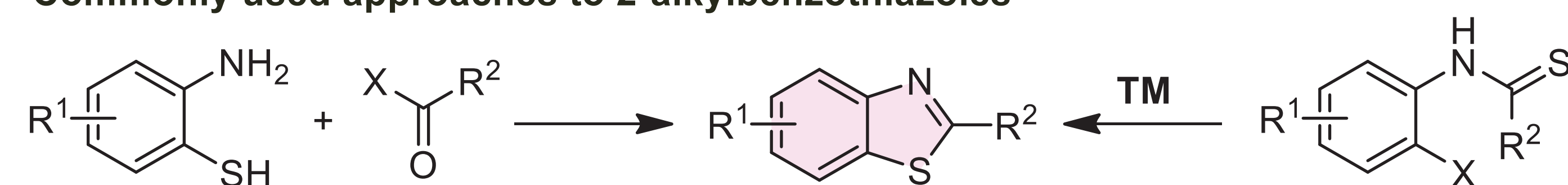
Volodymyr Puskov, Serhii Babii, Alexander Lyapunov, Dmytro Volochnyuk, Serhiy Ryabukhin

Background and the status quo of benzothiazole research

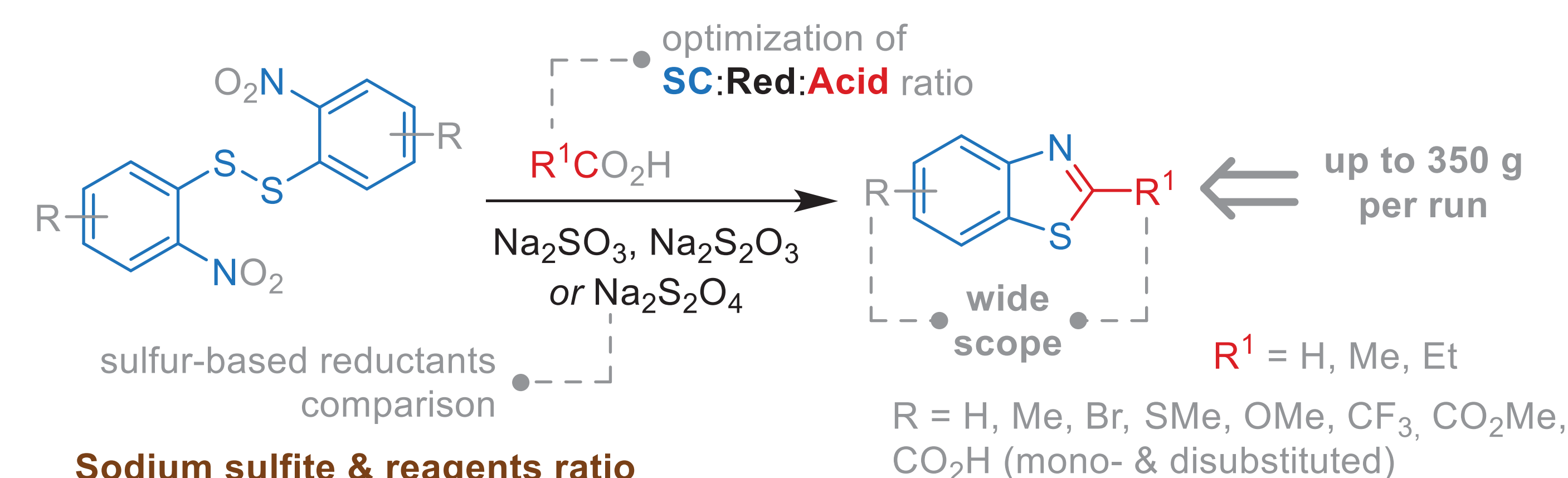
- 2-alkylbenzothiazoles are widely used as key precursors for dyes, photosensitizers, and fluorescent markers
- the compounds are demanded in multigram and even kilogram amounts



Commonly used approaches to 2-alkylbenzothiazoles



Optimization steps towards 2-alkylbenzothiazoles

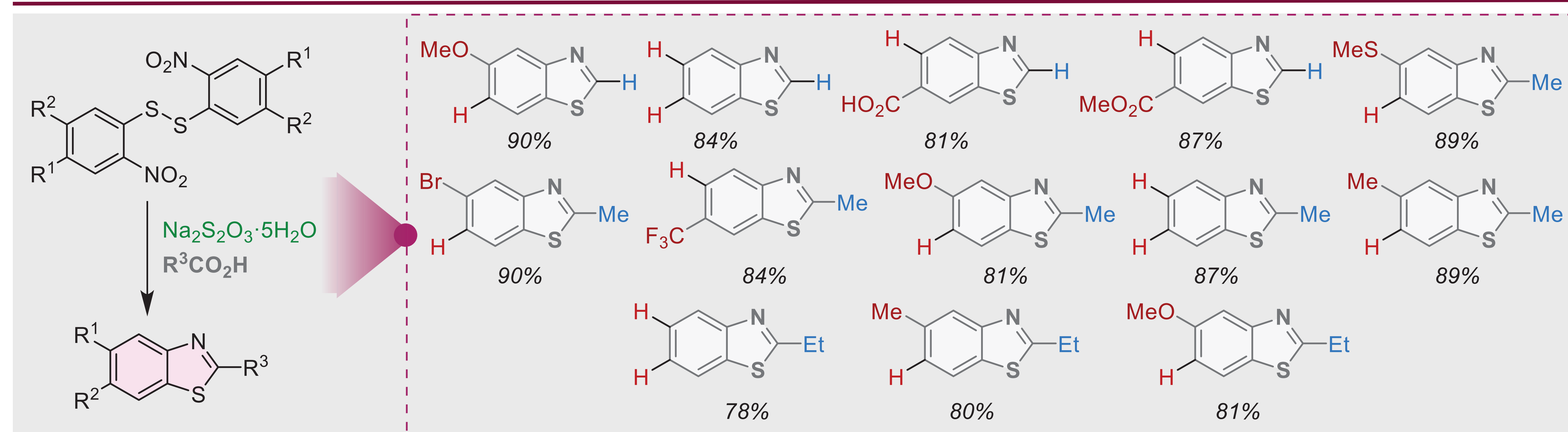


STEP A	v(disulfide) : v(Na ₂ SO ₃) : v(AcOH)				yield, %
	1:5:30	→	34		
	1:6:30	→	57		
	1:7:30	→	79		
	1:8:30	→	89		
	1:9:30	→	89		
	1:10:30	→	89		
STEP B	v(disulfide) : v(Na ₂ SO ₃) : v(AcOH)				yield, %
	1:8:22.5	→	89		
	1:8:20	→	89		
	1:8:17.5	→	89		
	1:8:15	→	83		
	1:8:12.5	→	70		
STEP B	Na ₂ SO ₃ : Na ₂ S ₂ O ₅ : Na ₂ S ₂ O ₄ : Na ₂ S ₂ O ₃ ·5H ₂ O				yield, %
	R ¹ = H, R ² = SMe	89	—	86	87
	R ¹ = H, R ² = OMe	17	—	89	90
	R ¹ = H, R ² = OMe	15	—	82	81
	R ¹ = H, R ² = OMe	23	—	88	89
	R ¹ = H, R ² = OMe	—	—	87	86
	R ¹ = H, R ² = OMe	n.d.	—	89	n.d.

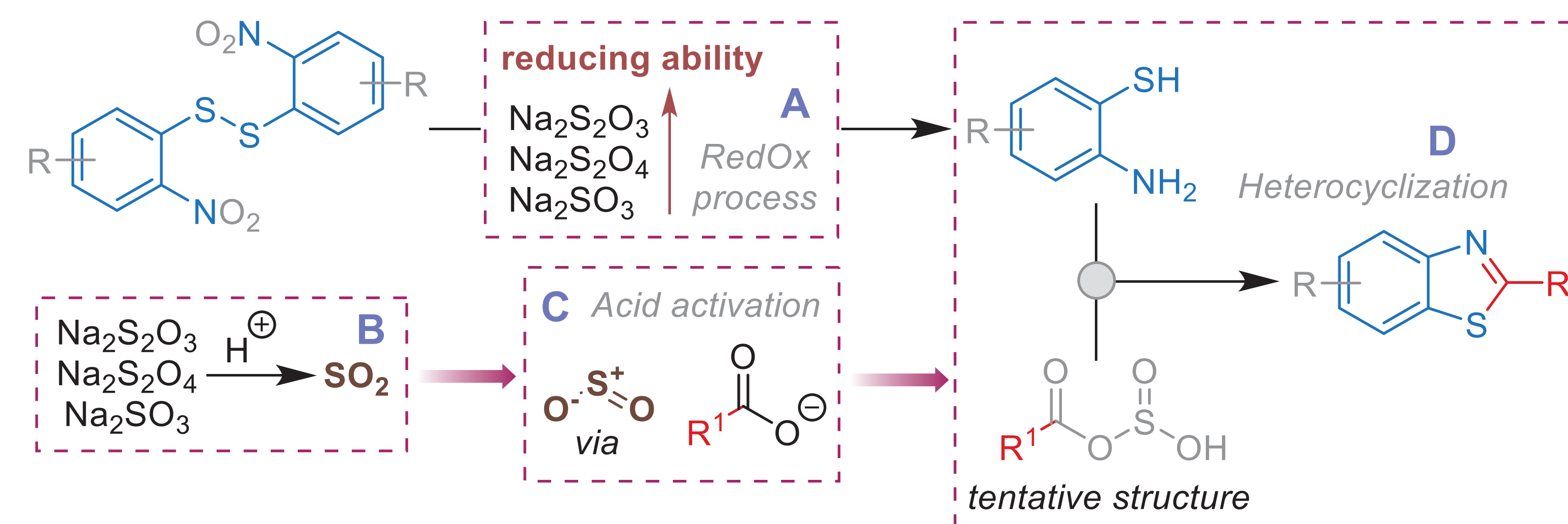
Contact

Serhiy V. Ryabukhin, Prof. Dr. Sci., s.v.ryabukhin@gmail.com
Dmytro M. Volochnyuk, Prof. Dr. Sci., d.volochnyuk@gmail.com

Synthetic results: Diversity of obtained products & mechanistic investigations



MECHANISTIC EXPLANATION: 4-STAGE PROCESS



MECHANISM STAGES

A: reduction of bis-(2-nitrophenyl)-disulfides into intermediate 2-aminothiophenols

B: generation of SO₂ from reductant in acidic media

C: activation of acid by SO₂

D: heterocyclization of 2-aminothiophenols with activated acid derivative into final benzothiazoles product

PROFILING A SAFE TEMPERATURE RANGE: THERMOGRAVIMETRY STUDIES

- the intervals for the potential thermal runaway decomposition for all compounds are in the range of 220–310°C
- CF₃-containing disulfide requires additional studies for designing industrial processes

